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The main theme of this proposal is the development of practical new techniques for stereocontrolled chemical glycosylation. As a result of the refinement of a new method for chemical glycosylation that we named HAD (H-bond-mediated Aglycone Delivery) method a number of therapeutically relevant compounds was obtained. Having obtained a range of synthetically challenging 1,2-cis linked oligosaccharides, we turned our attention to the development of glycosyl donors with switchable stereoselectivity. Among a variety of systems tested, we showed that if the nitrogen atom of the 2-O-picolinyl moiety is temporarily blocked by coordination to the metal center (Pd), it becomes unavailable to provide participation in glycosylation and hence the stereoselectivity of 2-O-picolinyl-assisted glycosylations can be "switched".